Gas Kinetics

Introduction

- Most deposition techniques rely on gas flow in a vacuum.
- We need a model for understanding;
  - the speed and energy of the gas molecules as a function of temperature and pressure,
  - how these molecules interact with each other and their surroundings,
  - and how mass, heat and momentum is transported by these molecules.

The Size of a Molecule
(a very rough calculation)

- Take water (liquid H_2O) as an example.
- Oxygen has 8 protons and 8 neutrons for a total of 16 nucleons and Hydrogen has 1 proton. So water has 16+1+1=18 nucleons

$$m_P \approx m_N \approx 1.66\times10^{-24}\,g$$

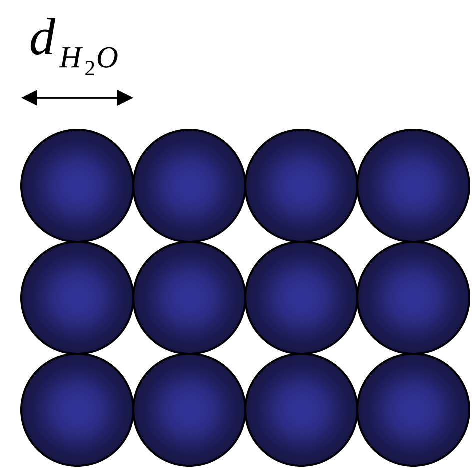
$$m_{H_2O} = 18 m_N = 2.99\times10^{-23}\,g$$

$$N_{H_2O} = 1/m_{H_2O} = 3.35\times10^{22}\,molecules/g$$

$$\rho_{H_2O} = 1.00\,g/cm^3$$

$$V_{H_2O} = \frac{1}{\rho_{H_2O} N_{H_2O}} = 2.99\times10^{-23}\,cm^3/molecule$$

$$d_{H_2O} = 2\times\sqrt[3]{\frac{3}{4}V_{H_2O}} = 5.64\times10^{-8}\,cm$$



The Distance Between Molecules in a Gas

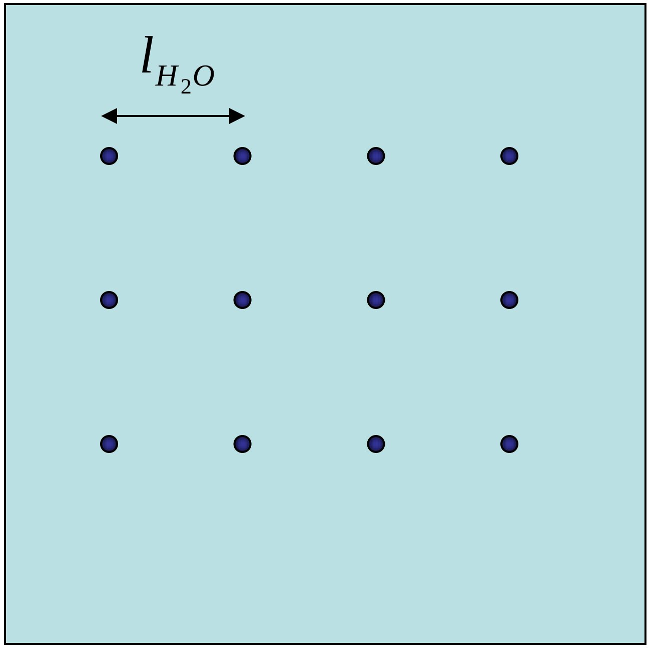
- Now take water vapor (gaseous H_2O).

$$\rho_{H_2O} = 0.8 \times 10^{-3} g / cm^3$$

$$V_{H_2O} = \frac{1}{\rho_{H_2O} N_{H_2O}} = 3.73 \times 10^{-20} cm^3 / molecule$$

$$l_{H_2O} = \sqrt[3]{V_{H_2O}} = 3.34 \times 10^{-7} cm$$

$$l_{H_2O} \approx 6 d_{H_2O}$$



Molecular Velocities

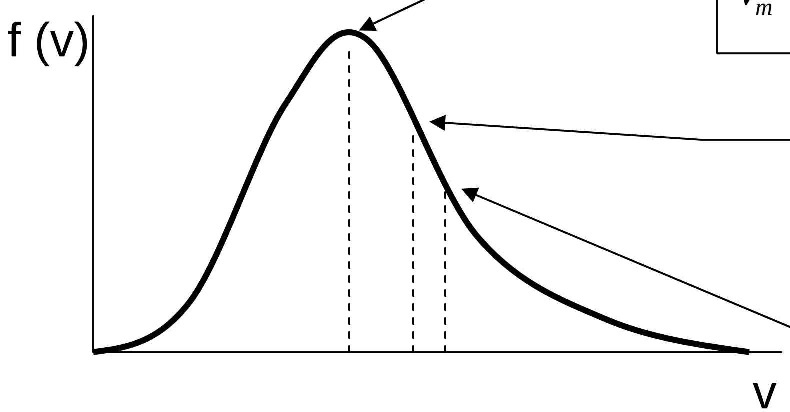
- Basic assumptions:
  - We'll assume an ideal gas where the gas molecules interact elastically (collisions are similar to the collisions of hard billiard balls).
  - The distance between molecules are large compared to their sizes.
  - There are no attractive or repulsive forces between the molecules and each molecule moves independently of the others.

Maxwell-Boltzmann Distribution

- Under these assumptions, the molecules of a gas have velocities that are distributed according to:

$$\boxed{f(v) = \frac{1}{n}\frac{dn}{dv} = 4\pi v^2 \sqrt{\frac{M}{2\pi RT}} \exp\left(-\frac{Mv^2}{2RT}\right)}$$

where *f* is the fractional number of molecules, *v* is the velocity, *M* is the molecular weight, *T* is the temperature and *R* is the universal gas constant.



$$\boxed{v_m = \sqrt{\frac{2RT}{M}}}$$ most probable speed

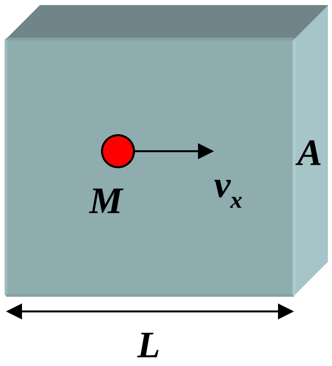
$$\boxed{\bar{v} = \sqrt{\frac{8RT}{\pi M}}}$$ mean speed

$$\boxed{v_{rms} = \sqrt{\frac{3RT}{M}}}$$ root mean speed

While the velocity of a single molecule depends on the temperature and its molecular weight, its kinetic energy is only dependent on temperature and is equally partitioned into the three coordinates.

Pressure

- Since readily measurable quantities are temperature and pressure (and not number density or velocity) we need a more convenient relationship that relates them.
- Pressure arises from the momentum transfer from the gas molecules to the walls of the container.
- The average force on the walls of the container is given by:



$$\overline{F} = MN_m \frac{\overline{v_x}^2}{L} = \frac{1}{3} MN_m \frac{\overline{v}^2}{L} = \frac{MN_m}{3L}\frac{3RT}{M} = \frac{N_m RT}{L} = \frac{N_m RTA}{V}$$

$$P = \frac{\overline{F}}{A} = \frac{N_m RT}{V}$$ then

$$\boxed{PV = N_m RT}$$ or $$\boxed{PV = Nk_B T}$$

where N_m is the total number of moles of the gas and N is the number of molecules

Units of Pressure

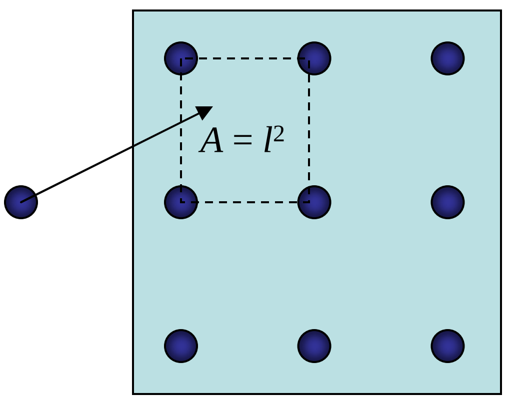
- SI units: 1 Pascal (1 Pa) = 1 N/m^2
  - Not very practical
- 1 Torr = 133 Pa = 1 mm Hg
- 1 bar = 750 Torr = 10^5 Pa = 0.987 atm
- 1 atm = 760 Torr = 10100 Pa
- 1 psi = 51.71 Torr = 0.068 atm

Mean Free Path

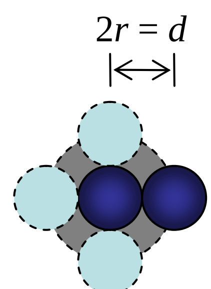
- In a vapor, gas molecules will be moving freely.
- Their motion is interrupted only by collisions with other molecules or the container.
- The average distance a molecule can move between collisions is called the mean free path.

Rough Calculation of the MFP

- Suppose there is a gas molecule trying to get through an array of gas molecules.



Area blocked by one molecule



Probability that a collision will occur

$$R = \pi d^2 / l^2$$

Average number of layers between collisions

$$1/2R = l^2 / 2\pi d^2$$

$$MFP = \frac{l}{2R} = \frac{l^3}{2\pi d^2} = \frac{1}{2\pi n d^2}$$

where n is the number of gas molecules per cm³

Rough Calculation of the MFP

In an ideal gas $n = \frac{N}{V} = \frac{P}{k_B T}$

$$MFP = \frac{1}{2\pi n d^2} = \frac{k_B T}{2\pi d^2 P}$$

More accurately $\boxed{MFP = \frac{\sqrt{2} k_B T}{2\pi d^2 P}}$

P (Torr)	MFP (cm)
760	10^{-5}
1	10^{-2}
0.001	10

Molecular Flow Regimes

- Since film deposition depends on how a gas flows and the mean free path is a measure of the interaction between the gas molecules, it determines the type of gas flow that can happen.
- The flow of gas is characterized by the **Knudsen number** (*Kn*).

$$\boxed{Kn = \frac{MFP}{L}}$$

L is a dimension of the vacuum chamber

- If *Kn* < 0.01, many molecules in chamber, pressure is high, the flow is <u>viscous</u> (like a fluid).
- If *Kn* > 1, few molecules in chamber, pressure is low, gas flow is <u>molecular and ballistic</u>.
- If 1 > *Kn* > 0.01, the gas is in a transition regime where neither property is valid.

Gas Transport: Diffusion

- Diffusion in gases is the mixing of one material (A) into another (B).
- Fick's Law for solids is still valid.

$$\boxed{J = -D\frac{dn_A}{dx}}$$

$$\boxed{D \propto \frac{T^{7/4}\sqrt{\frac{1}{M_A}+\frac{1}{M_B}}}{P\left(d_A+d_B\right)^2}}$$

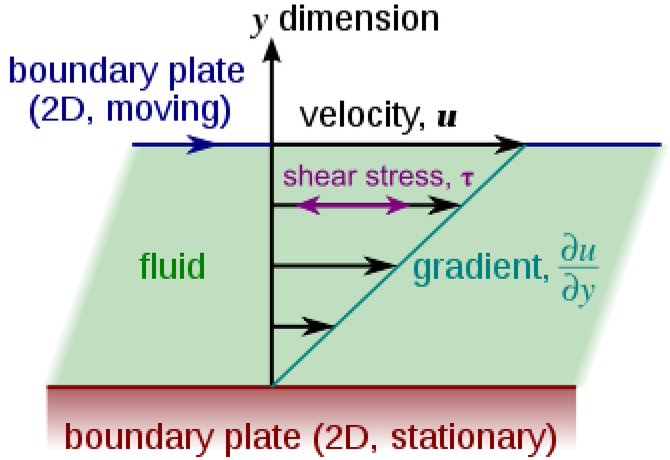
- In the ballistic regime (*Kn* > 1) diffusion will not occur (not enough molecules around).

Gas Transport: Viscosity

- In a chamber, gas molecules traveling at different speed exert drag on each other.

$$\boxed{\tau = \eta\left(\frac{du}{dy}\right)}$$

where, τ is the shear stress, *u* is the velocity in a direction perpendicular to *y and* η is the viscosity.



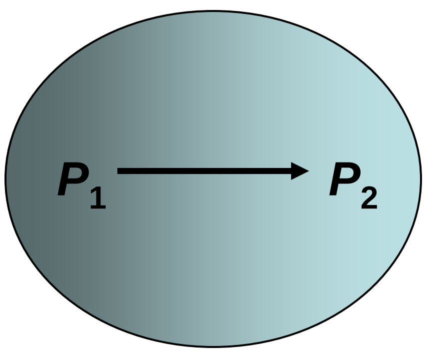
- Again, in the ballistic regime, viscous interactions do not occur.

Gas Transport: Heat Conduction

- Heat can be transported through the transfer of kinetic energy between gas molecules.
- In the viscous regime, heat transfer between a heater and the substrate occurs through the collisions of the gas molecules in between.
- In the ballistic regime, the molecules don't collide with each other so heat transfer depends on the amount of flow of molecules (flux) from the heater to the substrate.

Gas Flow

- Gas will flow when there is a pressure difference between different sections of a chamber.



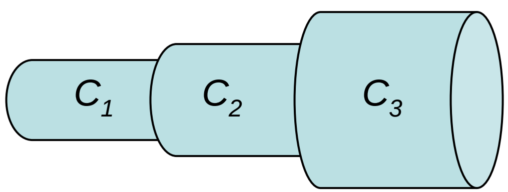
$$\boxed{Q = C\left(P_1 - P_2\right)}$$

Conductance (Lt/s) is shape dependent

Throughput

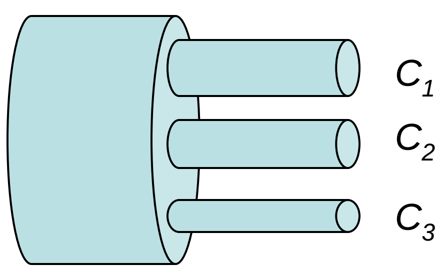
Conductance

- In a system with multiple components, the overall conductance is determined by how the components are hooked up.
- Series connections:



$$C_{sys} = \left(\frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} + \ldots \right)^{-1}$$

- Parallel connections:

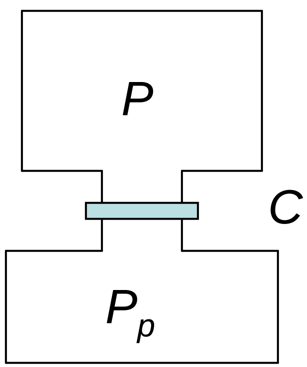


$$C_{sys} = C_1 + C_2 + C_3 + \ldots$$

Pumping Speed

- The pumping speed S_p, is defined as the volume of gas passing the plane of the inlet port per unit time when the pressure at the pump inlet is P_p.

$$\boxed{Q = P_p S_p}$$



Chamber

Pump

$$Q = C\left(P - P_p\right) = P_p S_p$$

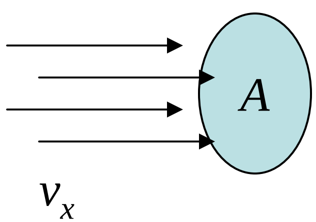
$$S_{eff} = \frac{Q}{P} = \frac{S_p}{1 + S_p / C}$$

Interaction With Surfaces

- Gas molecules colliding with the chamber walls result in pressure.
- Another possible interaction (and one crucial in film deposition) is gas impingement on other surfaces such as the substrate.
- A measure of the amount of gas incident on a surface is the flux.

Flux

- The flux is the number of molecules that strike an element of a surface perpendicular to a coordinate direction, per unit time and area.



$$\Phi = \int_0^\infty v_x \, dn_x \longrightarrow \frac{\Phi}{N_A} = \frac{P}{\sqrt{2\pi MRT}}$$

$$\boxed{\Phi = 3.513 \times 10^{22} \frac{P}{\sqrt{MT}}}$$

with *P* expressed in Torrs

Deposition Rate

- The flux of molecules on the surface leads to deposition where the rate of film growth depends on the flux.

$$\frac{dh_{film}}{dt} = \Phi\left(\frac{M_{film}}{\rho_{film} N_A}\right)$$

where M_{film} is the molar molecular mass (g/mol) and ρ_{film} is the film density (g/m^3)

- Of course this assumes that there are no chemical reactions, bouncing off of molecules or diffusion into the surface.